

DESULFURIZATION OF HOT COAL-GAS IN A HIGH-PRESSURE FLUID-BED REACTOR

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ABSTRACT

Zinc ferrite, a regenerable mixed-metal oxide, is a leading sorbent for removal of H_2S from hot coal-derived gas streams for integrated gasification combined cycle (IGCC) applications. The cyclic nature of the desulfurization process and the highly exothermic regeneration with air impose severe restrictions on the zinc ferrite process in a fixed-bed reactor. Due to several potential advantages of fluid-bed operation, a high-temperature high-pressure bench-scale reactor was constructed and commissioned for testing in the fluid-bed mode. Zinc ferrite ($192\ \mu m$ mean particle diameter) was tested at a superficial velocity to minimum fluidization velocity ratio of 3.0. Multicycle testing at 15 atm and $600^\circ C$ with 5000 ppmv H_2S in the inlet simulated fluid-bed coal gasifier (KRW) gas showed that zinc ferrite consistently reduced the H_2S to under 20 ppmv, in a single-stage fluidized bed at a superficial residence time of ~ 3 seconds. Prior to reaching a bed outlet H_2S concentration of 100 ppmv, a sulfur pickup of 12 g per 100 g sorbent was achieved.

INTRODUCTION

Integrated gasification combined-cycle (IGCC) and coal gasifier/molten carbonate fuel cell (MCFC) power systems employing hot-gas cleanup are two of the most promising advanced technologies for producing electric power from coal. High-temperature desulfurization at conditions that nearly match the pressure and temperature of raw coal gasifier gas has the potential to eliminate the requirements for expensive heat recovery equipment and efficiency losses associated with coal gas scrubbing (U.S. Department of Energy, 1986). High-temperature desulfurization research has focused on the development of mixed-metal oxide sorbents for fixed-bed reactor applications (Gangwal et al., 1989a, 1989b; Grindley and Steinfeld, 1985; Grindley and Goldsmith, 1987). The primary emphasis of this work has been on the development of a zinc ferrite sorbent (a mixed-metal oxide containing zinc oxide and ferric oxide in equimolar proportions) which is a leading candidate for demonstration under the Department of Energy's Clean Coal Program.

Fluid-bed reactors offer several potential advantages over fixed-bed reactors for high-temperature desulfurization of coal-gas. They provide excellent gas-solid contact via vigorous agitation of small particles and thereby also minimize diffusional resistances, give faster overall kinetics, and allow pneumatic transport. Fluidized beds prevent solids segregation at high temperature, offer the capability of continuously adding or removing sorbent, and allow control of highly exothermic sorbent regeneration reactions. It is the need for sorbent regeneration that actually imposes restrictions on fixed-bed technology because a true steady-state is hardly reached in the regenerator off-gas concentration. Fluidized-beds can also withstand a far greater particulate loading in the coal gasifier gas than can fixed-beds.

The objective of the study, motivated by the numerous advantages of fluid-beds, is to develop durable zinc ferrite sorbent formulations suitable for fluid-bed application and test them at conditions simulating coal gasifier gases at high-temperature

high-pressure (HTHP) conditions representative of advanced power plants. High-pressure applications of fluid-bed reactors for desulfurization based on lime and iron-oxide based sorbents have been carried out by Curran (1974) and Isshiki et al. (1987), respectively. The main inferences of significance based on these papers are (1) high attrition resistance of the sorbent will be required and (2) high hydrogen sulfide removal efficiency and stable operation will be possible at HTHP conditions. Our initial results of this on-going study to develop durable zinc ferrite sorbents are presented in this paper.

SORBENT PREPARATION

Zinc ferrite (ZnFe_2O_4) is formed by heating to temperatures $>816^\circ\text{C}$ (1500°F), an approximately equimolar mixture of zinc oxide (ZnO) and ferric oxide (Fe_2O_3) in the presence of a suitable binder such as bentonite. A solid-state reaction takes place giving ZnFe_2O_4 . A significant data base exists for fixed-bed formulations of this sorbent. The fixed-bed sorbents have been manufactured by AMAX (Jha et al. 1988) and United Catalyst, Inc. (UCI) as 3/16-inch cylindrical extrudates and spherical pellets. More recently, UCI has manufactured a number of zinc ferrite formulations for General Electric (GE) Co. (Ayala et al., 1989) by rounding out the cylindrical extrudates. The rounding process yields 1/8-inch to 3/8-inch ellipsoidal pellets which are believed to possess better attrition resistance in a moving bed because of elimination of sharp edges of the cylindrical extrudates. None of the sorbents manufactured to date is applicable to fluid-beds for which particle sizes on the order of 40 to 500 μm are needed.

Three methods were chosen to prepare fluid-bed zinc ferrite (1) crushing and screening of durable fixed-bed and moving-bed sorbents to desired particle size distribution, (2) spray drying, and (3) impregnating commercial fluidizable support materials such as alumina. The first method is obvious and gives high flexibility in the choice of the desired particle size distribution. However, it may not be the most viable commercial option because of the additional cost associated with crushing, screening, and recycling fines. The particulates formed may be angular with sharp edges which may be subject to high initial rates of attrition. Keeping this in mind, a modification of the first method consisted of fluidizing the crushed zinc ferrite to remove the sharp edges and round the sorbent. Commercially, fluidizable particles such as fluid-cracking catalysts (FCC) consisting of microspheroids are generally prepared by the second method, spray drying. This method, however, does not afford flexibility in particle size which are typically in the 20 to 150 μm range with a mean of about 80 μm . The third method chosen for investigation involved pore volume impregnation of commercially available fluidizable aluminas with a solution of zinc and iron nitrates in the required chemistry followed by drying and calcination at the desired temperature.

SORBENT CHARACTERIZATION

Sorbents were characterized using a variety of techniques prior to testing at the bench-scale. The most important sorbent characteristics included sulfur capacity (defined as grams of sulfur adsorbed per 100 grams of sorbent), regenerability and attrition resistance. Other sorbent properties of importance included mercury pore volume distribution, BET surface area, particle size distribution, weight % of ZnO , Fe_2O_3 , and binder, binder type, and x-ray diffraction (XRD) phase. Sorbent sulfur capacity and regenerability were measured by a thermogravimetric analyzer (TGA) using procedures similar to those developed for fixed-bed sorbents (Gangwal et al., 1989b; Gangwal and Harkins, 1989). The attrition resistance (A_p) of the sorbent was measured using an attrition tester similar to the one described by Anderson and Pratt (1985). Further details of the attrition tester and test procedure are available (Gangwal and Harkins, 1989). Briefly the attrition test consisted of flowing 5 slpm of N_2 for 1 hour through 50 cc of the sorbent in a 1.0-inch diameter quartz tube. The sorbent was supported on a plate with a single 0.4 mm diameter hole in the center. The N_2 emerged at very high velocity through the sorbent near the hole,

thus producing a vigorous shearing effect so that measurable differences in attrition could be produced between different sorbents in a relatively short time. For a sorbent of any particle size distribution, A_r was defined as $A_r = 100(1-B/A)$, where B was the increase in the fines (sizes below the smallest significant particle size) following the attrition test and A was the original amount of sorbent excluding the original fines. The attrition test was designed as a relative (rather than absolute) measure of the tendency of the sorbent to produce fines during fluidization.

BENCH-SCALE UNIT/TEST PROCEDURE

Theoretical modeling, construction of a high-pressure cold fluid-bed system (cold-flow model), and construction of the HTHP bench-scale unit was carried out. The theoretical modeling and the cold flow model were intended to aid in determining the desirable test conditions for the HTHP system. The theoretical modeling followed the approach of Cockrill et al. (1988) and used the bubbling-bed model. The objective of the modeling was to determine the amount of sorbent to be loaded in the reactor, given a set of pressure, temperature, sorbent capacity, gas composition, and sorbent physical properties, so that breakthrough to a level of 10% of the inlet H_2S concentration (0.5 volume %) could be achieved in a reasonable time while operating in the bubbling-bed regime and avoiding slugging.

The modeling was carried out using empirical literature correlations. Unfortunately, nearly all such correlations have been developed using atmospheric pressure test rigs. Thus as a further aid in evaluating fluidization behavior of the sorbents, avoiding slugging, and determining desirable test conditions, a see-through high-pressure apparatus (cold-flow model) was constructed. A commercial porous 1/4-inch thick α -alumina ceramic material with 16 μm pores was used as a distributor in this apparatus. The pipe was made from clear polycarbonate rated to >50 atm. Both 2-inch and 3-inch diameter models were constructed. Since the effect of temperature on fluidization was expected to be minimal, the cold-flow model provided tests of sorbent fluidization behavior which would be representative of the HTHP reactor.

An existing fixed-bed sorbent test facility (Gangwal et al., 1989b) was modified for fluid-bed operation. A schematic diagram of the facility is shown in Figure 1 and a more detailed diagram of the reactor is shown in Figure 2. The system was rated at 35 atm at 788°C (1450°F) and consisted of both 3-inch and 2-inch diameter sorbent cages. The same distributor material as the cold flow model was used. Separate lines and internal cyclones were provided for sulfidation and regeneration. The system provided high flexibility in the choice of gas composition and test conditions (flow rate, pressure, temperature, sorbent amount). The GC system (not shown) could analyze both inlet and outlet gases. Multiple detectors and valve switching arrangement provided for analysis of all permanent gases and sulfur gases. The H_2S , COS, and SO_2 could be analyzed at concentrations down to 0.1 ppmv every 2 to 6 minutes. All parts exposed to hot gases were Alon processed to prevent corrosion. Pressure drop across the bed was measured using a differential pressure gauge. A typical bench-scale test consisted of loading the desired amount of sorbent and bringing the unit up to the desired temperature and pressure. The amount of sorbent loaded in the reactor and the superficial velocity used was guided by preliminary modeling and preliminary tests on the cold flow model. Sulfidation gas of a composition typical of coal gasifier gas from a KRW (originally Westinghouse and now Kellogg) fluid-bed gasifier was then passed through the sorbent at superficial velocity (U_0) to minimum fluidization velocity (U_{mf}) ratio of about 3.0. Sulfidation was terminated when the outlet gas H_2S concentration reached around 500 ppmv (which was about 10% of the inlet H_2S concentration). Regeneration of the sorbent was then carried out with a gas containing 2% O_2 and 98% N_2 at maximum temperatures up to 760°C (1400°F) and similar U_0/U_{mf} ratio as sulfidation. Previous fixed-bed experience with zinc ferrite showed that 760°C was required to prevent sulfate formation. End of regeneration was indicated when SO_2 in the off-gas fell below about 200 ppmv. The sulfidation-regeneration cycle was then repeated as many times as desired. The sorbent was characterized before and after each test for its particle size distribution and attrition resistance (A_r).

RESULTS AND DISCUSSION

Sorbent preparation activities initially concentrated on spray-drying followed by rotary calcination at temperatures up to 1750°F. UCI conducted bench-scale and pilot-scale trials to produce a spray dried zinc ferrite comparable in attrition resistance to FCC material. Bench-scale trials used up to 20% binder consisting of bentonite, Al_2O_3 gel, SiO_2 gel, and TiO_2 . Two formulations (L-3392 with 15% binder and L-3393 with 20% binder) were prepared. The mean particle sizes of the L-3392 and L-3393 sorbents were 102 μm and 88 μm respectively. The attrition resistances of these sorbents were compared to a standard FCC material. Both L-3392 and L-3393 were subjected to greater attrition ($A_p \approx 70$ for L-3392 and L-3393 VS 97 for FCC) than FCC and thus were considered unacceptable for fluid-bed application. TGA tests of these sorbents showed very desirable capacity and reactivity, however. In order to increase attrition resistance, UCI increased the binder level to 25% and 50% in pilot-scale trials. In both cases agglomeration occurred and bricks rather than free-flowing particles were formed. The bricks were crushed and tested for attrition resistance. Although these materials showed high attrition resistance, they no longer possessed sulfur capacity as shown by the TGA. At this point UCI decided to terminate their effort to produce fluidizable zinc ferrite by spray drying.

With the failure of spray-drying as a potential technique, activities were initiated for sorbent preparation by impregnation. Commercial fluidizable γ -alumina and α -alumina powders were chosen for initial preparations. α -alumina was successfully loaded with up to 20 weight zinc ferrite. The procedure consisted of impregnating zinc and iron nitrates in a liquid volume equal to the pore volume of the alumina. This was followed by drying (120°C) and calcination at temperatures from 600°C to 840°C. The samples were tested for capacity by TGA. Sorbents calcined at temperatures up to 750°C quickly sulfided to their maximum capacity and were regenerable over 1.5 cycles, with no loss in capacity during the second cycle. The sample calcined at 840°C did not attain maximum capacity. Tests were not successful with the γ -alumina which showed poor reactivity presumably due to a strong chemical interaction of the reactive alumina with the active ZnO and Fe_2O_3 . The attrition resistance of the impregnated α -alumina zinc ferrite was somewhat less than a zinc ferrite prepared simply by crushing and screening a zinc ferrite prepared as ellipsoids for moving bed applications as discussed below.

Other potential methods, including modification of the impregnation method, are presently being investigated for producing a durable zinc ferrite sorbent. To initiate bench-scale testing, it was decided to select one of the available moving bed sorbents and prepare the desired particle size sorbent by crushing and screening. UCI had recently prepared a 20,000 lb batch of zinc ferrite designated T-2465M for GE. The properties of this sorbent are shown in Table 1. The low pore volume (0.2 cc/g) and high density (2.57 g/cc) of this sorbent compared to other sorbents (Ayala et al., 1989) made it a good candidate for testing in the fluid-bed mode. The sorbent was obtained from GE and crushed and screened to give a particle size distribution from -48 to +150 mesh (105 to 297 μm).

The results of two 10-cycle tests conducted with the T-2465M sorbent are reported herein. Both tests were conducted without a cyclone. Test 1 was conducted using the 2-inch diameter sorbent cage with 179 grams of the sorbent, whereas Test 2 was conducted with the same cage but with twice as much sorbent. The nominal conditions of the tests are shown in Table 2. U_{mf} was calculated using standard correlations presented by Kunii and Levenspiel (1969). The U_0/U_{mf} ratio of ~ 3.0 was guided by experiments at 15 atm in the cold flow model which showed a vigorously bubbling bed at U_0/U_{mf} of 2.6 and slightly slugging bed at U_0/U_{mf} of 3.0. The first cycle H_2S breakthrough curves for the two tests are presented in Figure 3. As can be seen, doubling the contact time improves the cleanup efficiency significantly. Estimated superficial contact time for Test 1 was ~ 1.6 seconds whereas that for Test 2 was ~ 2.9 seconds. The superficial contact time is calculated by dividing the estimated

expanded bed height (approximately 1.3 times the static bed height) by the superficial velocity. The static bed height is estimated from the particle density of 2.57 g/cc with the assumption of 40% voids in the bed. The results suggest that ~2.9 second superficial contact time is sufficient to obtain high cleanup efficiency in a single-stage fluid-bed.

The reason for using 179 g of sorbent for the first test was because this amount was indicated by modeling, following the approach of Cockrill et al. (1988) and using Kunii and Levenspiel's bubbling bed model. It was calculated that a breakthrough time (defined as the time to reach an outlet H₂S concentration equal to 10% of the inlet) of about 2 hours will be required. The actual breakthrough time from Figure 3, however, was only 0.5 hours. The model calculations had assumed an infinitely fast intrinsic rate constant. TGA tests, however, suggest that the intrinsic rate of reaction, in addition to gas and emulsion phase mass transfer rates, could represent a resistance to reaction. Also, product layer diffusion resistance through the -48 to +150 mesh particles could be important as shown by the TGA and could account for the flattening of the breakthrough curve for Test 1 past 50 minutes. The model is presently being refined based on the TGA results.

The sulfur capacity at a breakthrough level of 500 ppmv H₂S for each of the 10 cycles of Test 2 is shown in Figure 4. The sorbent is seen to retain a significant portion of its capacity over 10 cycles. The sorbent was subjected to particle size distribution measurement and attrition testing before and after each test. These results, shown in Table 3, indicate that fines continue to be created over the 10 cycles for both tests. Attrition resistance of the sorbent following testing appears to decrease with increased bed height. The reason for this may be increased particle-particle interaction in a deeper bed. The attrition resistance of the freshly crushed and screened T-2465M sorbent is similar to commercial fluidizable aluminas, as indicated earlier. The reduction in attrition resistance over 10 cycles is believed to be due to thermal cycling and chemical transformations during sulfidation and regeneration.

CONCLUSIONS

A zinc ferrite sorbent reduced the H₂S in coal gasifier gas to less than 20 ppmv in a single stage fluidized-bed at HTHP conditions. Crushing and screening of a durable ellipsoidal 1/8-inch to 3/8-inch zinc ferrite sorbent (T-2465M) produced a reasonable 192 μ m fluid-bed media whose initial attrition resistance was comparable or better than commercial fluidizable aluminas. The sorbent needs to be tested over a large number of cycles (~100) to further assess its durability under fluidizing conditions.

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Table 1. Properties of Sorbent T-2465M

ZnO : 34.0%	Pellet density : 2.57 g/cm ³
Fe ₂ O ₃ : 64.0%	Surface area : 4.6 m ² /g
Bentonite : 2.0%	Pore volume : 0.2 cm ³ /g
Size : 1/8 to 3/8 inch	Mean pore diameter : 1958 Å
Shape : ellipsoidal	Crush strength : 22.5 lb/pellet
Calcination Temperature : 843°C (1550°F)	Attrition resistance : 95.4%
Bulk Density : 1.44 g/cm ³	Theoretical sulfur capacity : 39 g/100 g

Table 2. Nominal Bench-Scale Test Conditions (Reactor I.D. = 2.0-inch)

	<u>Sulfidation</u>		<u>Regeneration</u>
Pressure (atm)	15		15
Temperature (°C)			
Maximum	630		760
Inlet	600		675
Average	615		Not applicable
Gas composition (vol. %)	<u>Inlet</u>	<u>Outlet</u>	<u>Inlet</u>
H ₂	9	13	--
CO ₂	5	9	--
H ₂ O	19	15	--
H ₂ S	0.45	0.001	--
N ₂	Balance	Balance	98.0
CO	16	12	--
O ₂	--	--	2.0
Flow (slpm)	35.0		32.0
U _{mf} (cm/s)	2.0		1.8
U _o * (cm/s)	6.2		6.1
U _o /U _{mf}	3.1		3.4

*Based on average temperature for sulfidation; inlet temperature for regeneration.

Table 3. Particle Size Distribution (Weight %) and Attrition Resistance (A_R) of Fresh and Used T-2465M Sorbent

	Fresh T-2465M	<u>Test 1 after</u>		<u>Test 2 after</u>	
		4 cycles	10 cycles	6 cycles	10 cycles
Size (μm)					
>297	0.00	0.02	0.34	0.79	0.08
250 to 297	13.46	8.27	4.59	13.14	11.36
177 to 250	44.87	43.36	43.19	37.42	37.81
149 to 177	10.43	12.03	11.63	11.46	10.71
125 to 149	24.07	17.48	18.50	18.47	19.58
105 to 125	7.16	13.06	14.53	13.85	13.41
<105	0.00	5.77	7.22	4.87	7.04
Average size (μm)	192	181	171	184	180
A _R	94.1	--	85.4	--	78.4

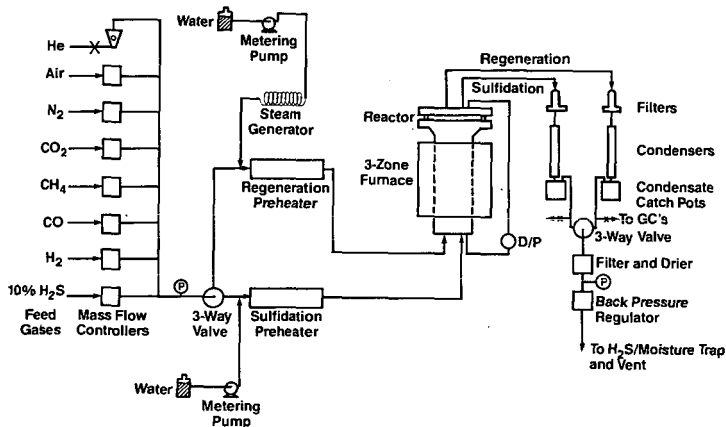


Figure 1. Bench-scale fluid-bed sorbent test facility.

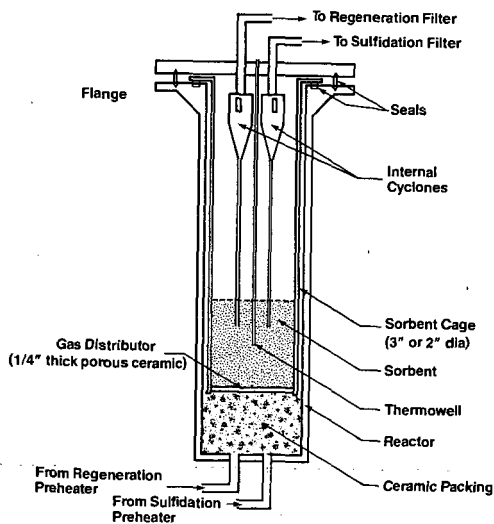


Figure 2. Fluid-bed reactor.

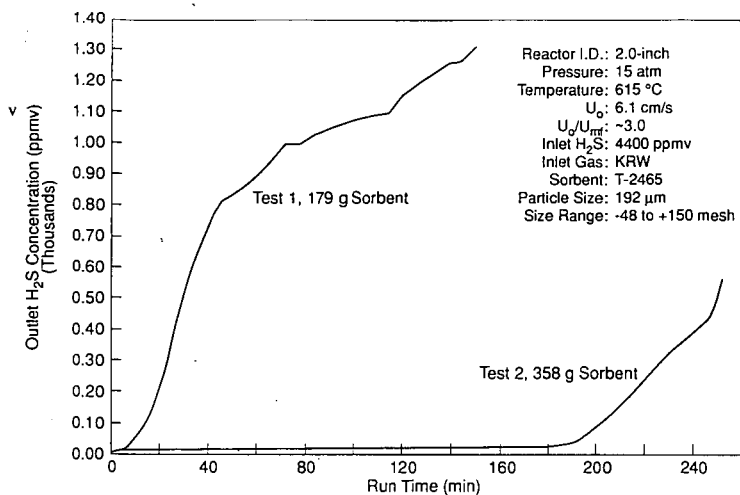


Figure 3. Effect of sorbent amount on H_2S breakthrough profile.

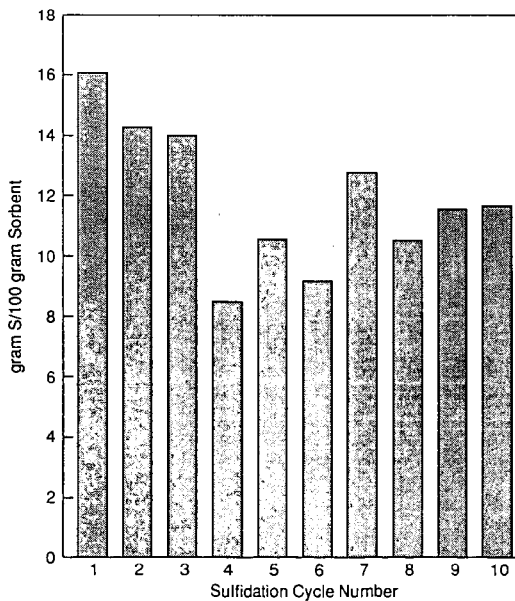


Figure 4. Sulfur capacity at 500 ppmv H_2S in outlet gas for Test 2 over 10 cycles (inlet H_2S = 4400 ppmv).